The Nature of Nonbonded Interactions between Divalent Selenium and Sulfur: a Theoretical Investigation

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Abstract

The nature of selenium-sulfur non-bonding interactions in a series of substituted benzeneselenenyl derivatives has been investigated by means of computational techniques. The results of these calculations, together with experimental measurements (X-rays crystallography and NMR), suggest that the strength of this interaction increases with the increase of electronegativity of the substituent on selenium. Natural bond orbital (NBO) analysis suggests that this interaction has a mainly covalent character, rather than electrostatic, and originates from an interaction between a lone pair of sulfur and an antibonding orbital on selenium. Atom in molecules (AIM) analysis further supports this finding.

Keywords: density functional calculations, nonbonded interactions, selenium, sulfur, natural bond orbital analysis, atoms in molecules

1. Introduction

Noncovalent bonding interactions are of fundamental importance in a variety of biological and chemical processes.[1] Secondary and tertiary structures of proteins for example are largely determined by these interactions, as well as their functions. Moreover most of the known drugs act forming weak noncovalent interactions in specific locations of their biomolecular target. Supramolecular chemistry is essentially based on multiple and reversible weak nonbonded interactions.[2] In fact even if the energy related to a single weak interaction is usually too small to determine macromolecular or supramolecular behaviors, the establishing of several cooperative interactions can have a relevant effect. The most important noncovalent bonding interactions are hydrogen bonding, ionic bond, ion-dipole interactions, dipole-dipole interactions, π-π interactions and van der Waals forces.

Another important class of nonbonded interactions is known to exist between chalcogen centers and hydrogen[3] or heteroatoms (chalcogens,[4] oxygen[5], nitrogen[6] and halogens[7]). The existence of this interaction has been demonstrated by means of X-rays crystallography, NMR techniques and computational methodologies. Particularly Se···O, Se···N and Se···Halogens interactions have been studied in great details.

There have been several reports on the importance of these interactions in determining the biological activity of organoselenium compounds. Particularly interesting are the cases of ebselen and its analogues as glutathione peroxidase (GPx) mimics and of selenazafurin as an antiinflammatory drug.[8] It has been demonstrated that in GPx mimics the presence of a Se···Het (particularly Se···N) interaction is responsible for the stabilization of a key intermediate in the catalytic cycle, the selenenic acid.[9]

In a different context the existence of this interaction has been proved to be fundamental for the transfer of chiral information in reactions mediated by optically active electrophilic selenenylating reagents.[10] Most of these compounds share common structural features: an aromatic ring with the

electrophilic selenium directly bound and an aliphatic chain in *ortho* position to selenium possessing both the stereogenic center and an heteroatom (O, N, Se, halogens). The existence of an interaction between the heteroatom (O, N, halogens) and the electrophilic selenium in these compounds has been proved by means of X-rays crystallography, NMR and computations and has been demonstrated to arise from an orbital interaction between a lone pair of the heteroatom (n_{het}) and the antibonding orbital formed by the selenium atom and the group directly bound to selenium (σ^*_{Se-X}).

A few years ago some of us introduced the first sulfur-containing chiral electrophilic selenenylating reagents.[11] These proved to be very efficient in a series of selenofunctionalizations as well as selenocyclizations, when compared to nitrogen or oxygen containing reagents. Recently we reported several experimental data suggesting the existence of a strong Se···S interaction in some of these compounds (**1-3**, Scheme 1). Compounds **1** and **2** were obtained as crystals and subjected to X-rays analysis that showed a surprisingly short Se-S distance (2.344 Å for chloride **1** and 2.497 Å for bromide **2**). Together with the upfield shift observed in ^{77}Se-NMR spectra already reported for similar systems, interestingly downfield shifts were observed in ^{1}H- and ^{13}C-NMR signals related to sulfur-bound methyl and methine groups. NOESY experiments further supported these findings, suggesting that this interaction exists also in solution (CDCl$_3$) and increases the conformational rigidity.[12]

Considering the increased availability of high level computational techniques and the lack of studies on Se-S nonbonding interactions we decided to investigate this topic using our previously reported electrophilic reagents as models as well as the related diselenide **4** and methylselenide **5**.

1: X=Cl
2: X=Br
3: X=I
4: X=SeMe
5: X=Me
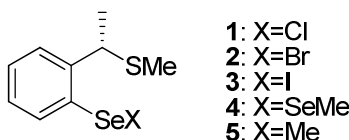
Scheme 1

2. Computational details

DFT calculations with B3LYP,[13] PBE96[14] and M06-2X[15] functionals have been performed using GAMESS-US[16] while for B2PLYP-D[17] calculations Orca[18] has been used. All optimizations have been performed without any constrain. All stationary point were characterized as minima by corresponding Hessian indices. The orbital interaction energies between Se and S as well as the atomic charges were calculated by using the natural bond orbital (NBO)[19] method on optimized structures at the same level of theory used for geometry optimizations. The atoms in molecules (AIM)[20] analysis was performed using Aimall[21] program. Topological properties were characterized on optimized structures at the same level of theory used for geometry optimizations.

3. Results and discussion

To understand how different substituents on selenium influence the strength of Se-S interaction five different compounds (**1-5**) were considered in our study. The choice of these compound has been done considering the availability of experimental data in order to be able to relate experimental and calculated results. Compounds **1-3** and **5** were synthesized and studied by NMR spectroscopy in a previous report,[12] while compound **4** was chosen as a model system for the related symmetrical diselenide. Density functional studies were carried out using five combinations of functionals and basis sets. Together with the well established B3LYP and PBE96 functionals we decided to use also the recently introduced M06-2X, which among the new Truhlar's functionals performs best in the study of noncovalent interactions,[22] and B2PLYP-D, a double hybrid density functional with the inclusion of dispersion correction. A combination of Huzinaga's 43321/4321/311 basis sets for Se and Br, Huzinaga's 433321/43321/4211 basis set[23] for I and 6-31G(d,p) for all other atoms (here called BS1) has been used in this study. Even if this combination proved to be very effective in previous reports[4f-h,7a] we performed calculations also using 6-311G(d,p) for all atoms in order to

validate our choice. The results of unconstrained geometry optimizations are summarized in Table 1.

Compound		B3LYP/6-311G(d,p)	B3LYP/BS1	PBE96/BS1	M06-2X/BS1	B2PLYP-D/BS1
1	$r_{Se\cdots S}$[a]	2.770	2.786	2.700	2.820	2.799
	$\theta_{S\cdots Se\text{-}X}$[b]	177.5	177.7	178.9	175.8	176.7
	$\omega_{Ar\text{-}Se}$[c]	-158.6	-158.4	-161.4	-155.7	-157.4
	$\omega_{Ar\text{-}C}$[d]	-39.5	-39.7	-38.8	-42.2	-41.4
2	$r_{Se\cdots S}$[a]	2.821	2.808	2.722	2.842	2.815
	$\theta_{S\cdots Se\text{-}X}$[b]	177.3	177.5	179.5	175.8	176.6
	$\omega_{Ar\text{-}Se}$[c]	-157.4	-157.2	-160.3	-154.3	-155.7
	$\omega_{Ar\text{-}C}$[d]	-41.5	-40.6	-39.7	-42.9	-42.3
3	$r_{Se\cdots S}$[a]	2.887	2.867	2.766	2.957	2.879
	$\theta_{S\cdots Se\text{-}X}$[b]	175.3	175.0	177.7	172.4	174.6
	$\omega_{Ar\text{-}Se}$[c]	-154.7	-154.0	-158.3	-148.3	-152.0
	$\omega_{Ar\text{-}C}$[d]	-44.0	-42.9	-41.2	-46.7	-44.4
4	$r_{Se\cdots S}$[a]	3.204	3.182	3.047	3.227	3.185
	$\theta_{S\cdots Se\text{-}X}$[b]	177.5	177.8	179.0	172.7	175.5
	$\omega_{Ar\text{-}Se}$[c]	-156.1	-156.1	-160.5	-149.8	-153.2
	$\omega_{Ar\text{-}C}$[d]	-52.4	-51.2	-47.4	-53.8	-52.1
5	$r_{Se\cdots S}$[a]	3.578	3.559	3.399	3.453	3.522
	$\theta_{S\cdots Se\text{-}X}$[b]	166.9	168.0	170.9	166.0	163.1
	$\omega_{Ar\text{-}Se}$[c]	143.3	144.3	147.5	141.2	137.8
	$\omega_{Ar\text{-}C}$[d]	74.9	74.1	69.3	70.1	72.9

[a] Se-S distance in angstrom; [b] S···Se-X bond angle in degrees; [c] Dihedral angle of the X-Se-C-C_C linkage in degrees; [d] Dihedral angle of the S-C-C-C_{Se} linkage in degrees.

Table 1 Summary of structural parameters from DFT calculations at various level of theories

The very similar results obtained with B3LYP functional and 6-311G(d,p) or BS1 basis sets justify the use of the latter in order to save computational resources.

In all the cases Se-S distances in chloride **1** and bromide **2** are significantly longer when compared to those obtained by X-rays analysis. This discrepancy can be due to intermolecular interactions in the solid state, as previously explained for related hypervalent selenium compounds.[24] Most notably the hybrid meta-GGA M06-2X functional provided the most different results from the experimental values. As expected shorter Se-S distances are predicted for molecules with more electronegative substituents on selenium, with this distance increasing in the order ArSeCl (**1**) > ArSeBr (**2**) > ArSeI (**3**) > ArSeSeMe (**4**) > ArSeMe (**5**). Anyway for all the molecules Se-S distances are shorter than the sum of van der Waals radii [vdw(Se) + vdw(S) = 1.90 + 1.80 = 3.70 Å). The selenium-

heteroatom distance has been often correlated to the existence and to the strength of a nonbonding interaction evaluating the covalency factors (χ).[4f,6b,25] These have been calculated based on interatomic distances obtained form X-rays analysis as well as geometry optimizations and are summarized in Table 2. A comparison of these values with those obtained for similar systems with Se-O (2-(Methoxymethyl)benzeneselenenyl chloride)[4f] or Se-N (2-(Dimethylaminomethyl)benzeneselenenyl chloride)[6b] nonbonding interaction suggests that the strength of Se-S interaction lies in between the strengths of Se-O ($\chi = 0.554$) and Se-N ($\chi = 0.705$) interactions.

	ArSeX				
X	X-Rays	B3LYP/BS1	B3LYP/6-311G(d,p)	PBE96/BS1	B2PLYP-D/BS1	M06-2X/BS1
Cl	0.935	0.630	0.641	0.690	0.621	0.607
Br	0.830	0.615	0.606	0.674	0.610	0.592
I	-	0.574	0.560	0.644	0.566	0.512
SeMe	-	0.357	0.342	0.450	0.355	0.326
Me	-	0.097	0.084	0.207	0.122	0.170

Table 2 Covalency factors calculated with Se-S distance obtained from X-rays analysis and DFT calculations

Another interesting aspect of the geometries summarized in Table 1 is the linearity of S···Se-X angle. This angle is always very close to 180° for compounds **1**-**4** and it only deviates significantly from linearity in compound **5**, for which the nonbonding interaction is expected to be weaker. This evidence suggests that also in these cases the main contribution to the stabilizing interaction relies on an orbital interaction rather than on an electrostatic one.

Since the Se-S distance has been previously considered as a measure of the strength of the nonbonding interaction and considering that ^{77}Se-NMR chemical shifts have been long known to be influenced by this interaction their correlation is plotted in Figure 1.
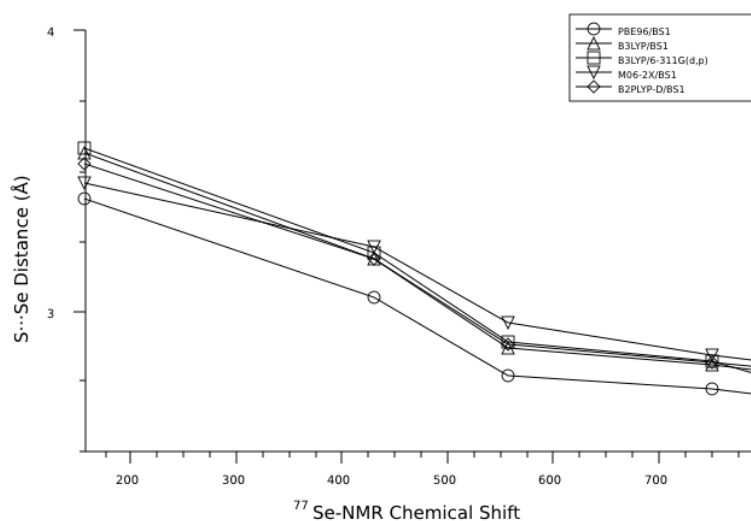

Figure 1 Plot of S-Se distance versus ^{77}Se-NMR chemical shifts

Linearity is observed at all the levels of theory and this further supports the hypothesis of the existence of this interaction and the dependence of its strength from the electronegativity of the

substituent on selenium center.

In order to obtain a deeper comprehension of the nature of Se-S interaction NBO and atoms in molecules (AIM) analyses have been performed on compounds **1-5** with the five combinations of density functional and basis sets used also for geometry optimizations. The main results are summarized in Table 3. This approach has been used by other authors in the investigations of Se-heteroatom interactions in related systems,[6] and thus can allow a direct comparison of our findings with previously published results.

	Compound	$E_{Se\cdots S}{}^{a}$ (kcal/mol)	$q_S{}^{b}$ (e)	$q_{Se}{}^{b}$ (e)	$\rho_{Se\cdots S}{}^{c}$ $(ea_0{}^{-3})$	$\rho_{rcp}{}^{d}$ $(ea_0{}^{-3})$	$\nabla^2\rho_{Se\cdots S}{}^{e}$ $(ea_0{}^{-5})$	$H_{Se\cdots S}{}^{f}$ $(ea_0{}^{-4})$
	B3LYP/6-311G(d,p)	39.02	0.32706	0.35270	0.040	0.017	0.060	-0.0052
	B3LYP/BS1	37.18	0.33904	0.40732	0.038	0.016	0.064	-0.0038
1	PBE96/BS1	42.07	0.38126	0.38410	0.046	0.018	0.065	-0.0068
	M06-2X/BS1	36.12	0.31930	0.45851	0.035	0.017	0.063	-0.0032
	B2PLYP-D/BS1	39.70	0.31157	0.45797	0.036	0.016	0.066	-0.0033
	B3LYP/6-311G(d,p)	34.83	0.31461	0.29457	0.036	0.016	0.058	-0.0039
	B3LYP/BS1	36.07	0.33506	0.33216	0.037	0.010	0.063	-0.0034
2	PBE96/BS1	40.58	0.38087	0.31161	0.045	0.011	0.064	-0.0061
	M06-2X/BS1	35.41	0.32063	0.37483	0.034	0.016	0.062	-0.0029
	B2PLYP-D/BS1	39.22	0.31362	0.37336	0.035	0.016	0.065	-0.0031
	B3LYP/6-311G(d,p)	29.43	0.30923	0.18734	0.032	0.016	0.055	-0.0027
	B3LYP/BS1	31.50	0.33092	0.21887	0.033	0.015	0.061	-0.0022
3	PBE96/BS1	37.37	0.37840	0.19947	0.041	0.017	0.063	-0.0048
	M06-2X/BS1	25.51	0.29972	0.25848	0.028	0.015	0.057	-0.0010
	B2PLYP-D/BS1	33.13	0.30366	0.25720	0.032	0.016	0.063	-0.0019
	B3LYP/6-311G(d,p)	8.13	0.22086	0.17299	0.017	0.011	0.042	0.0005
	B3LYP/BS1	9.52	0.24839	0.19459	0.018	0.011	0.045	0.0007
4	PBE96/BS1	12.83	0.28183	0.19629	0.024	0.013	0.052	-0.0002
	M06-2X/BS1	8.17	0.25014	0.21725	0.016	0.012	0.043	0.0008
	B2PLYP-D/BS1	9.72	0.24182	0.21173	0.018	0.012	0.046	0.0008
	B3LYP/6-311G(d,p)	1.00	0.18489	0.33448	no BCP or RCP			
	B3LYP/BS1	1.33	0.21492	0.37509	no BCP or RCP			
5	PBE96/BS1	2.82	0.22868	0.39012	0.012	0.011	0.033	0.0011
	M06-2X/BS1	2.70	0.23516	0.40257	0.010	0.010	0.032	0.0010
	B2PLYP-D/BS1	2.10	0.22185	0.38030	no BCP or RCP			

[a] The orbital interaction energy between the sulfur lone pairs (n_S) and the antibonding orbital (σ^*_{Se-X}) determined by NBO second-order perturbation analysis. [b] The atomic charge of the selenium or sulfur atom determined by NBO analysis. [c] The electron density at the BCP. [d] The electron density at the RCP. [e] The Laplacian of the electron density at the BCP. [f] The total energy density at the BCP calculated as $H=G+V$, where the G and V correspond to a local kinetic and potential energy density, respectively.

Table 3 Summary of NBO and AIM calculations

A confirmation of the existence of the Se-S interaction comes from the observation of stabilization energies due to the $n_S \rightarrow \sigma^*_{Se-X}$ orbital interaction obtained by NBO second-order perturbation

analysis. This interaction results to be strongly stabilizing for compounds **1**-**3**, while its relevance is only modest in diselenide **4** and can be neglected in the methylselenide **5**. The correlations between this orbital interaction energy and Se-S distance ($r_{Se\cdots S}$) is depicted in Figure 2.

This correlation clearly shows how a decrease in Se-S distance leads to a in increase in the orbital interaction between the lone pairs of sulfur and the antibonding orbital of Se-X bond. A similar correlation exists between the interaction energy and the covalency factors (Figure 3). The higher calculated energies correspond to higher covalency factors.
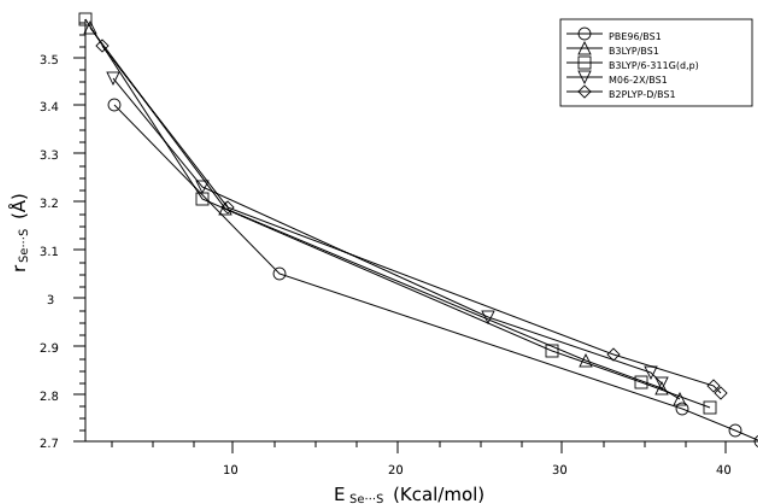
Figure 2 Plot of selenium-sulfur distance ($r_{Se\cdots S}$) versus second-order perturbation energy ($E_{Se\cdots S}$)
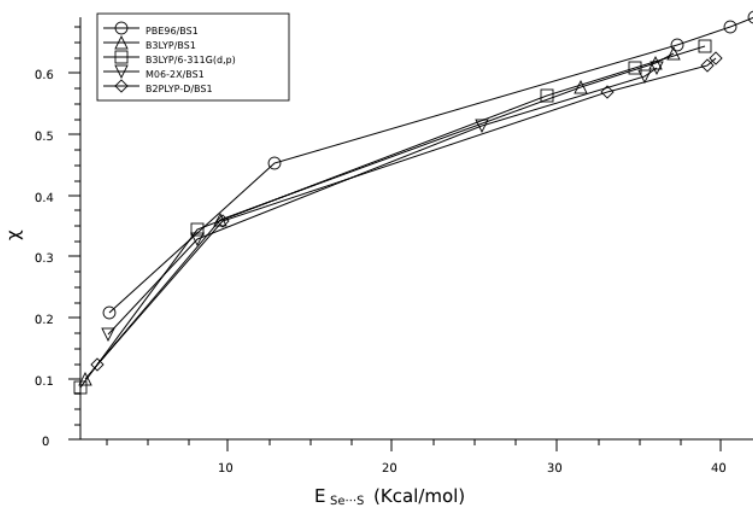
Figure 3 Plot of covalency factors versus second-order perturbation energy ($E_{Se\cdots S}$)

A deeper insight into the nature of Se-S nonbonding interaction comes from the analysis of net atomic charges as calculated by natural population analysis (NPA) (see Table 3). Surprisingly both selenium and sulfur are positively charged in all compounds and at all the considered level of theories, suggesting that the stabilization only depends on orbital interaction. This is in contrast to previous reported results on related oxygen or nitrogen containing compounds, in which a significative electrostatic contribution to nonbonding interaction was found. This statement is

further confirmed by the correlation of $E_{Se\cdots S}$ with the electron density at bond critical points ($\rho_{Se\cdots S}$) obtained by AIM analysis (Figure 4; Table 3 for numerical data). In AIM theory chemical bonding can be identified by the presence of a bond critical point (bcp), where the electron density reaches a minimum along the bond path. The presence of a bcp between selenium and sulfur was observed in compounds **1**-**4**, while for compound **5** only two of the five considered level of theories find a bcp, even if with very low electron density. The almost linear relationship between $E_{Se\cdots S}$ and $\rho_{Se\cdots S}$ (Figure 4) supports the suggestion of a dominant covalent character in the Se$\cdots$S interaction. The value of $\rho_{Se\cdots S}$ decreases in the order ArSeCl (**1**) > ArSeBr (**2**) > ArSeI (**3**) > ArSeSeMe (**4**) > ArSeMe (**5**), similarly to $E_{Se\cdots S}$.
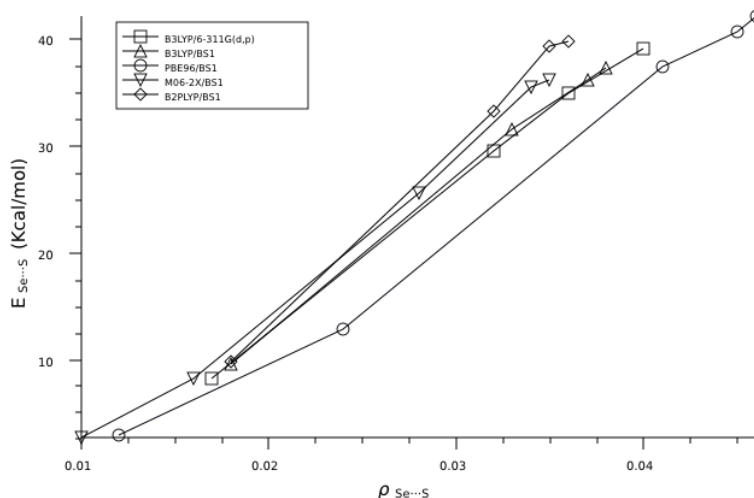

Figure 4 Plot of second-order perturbation energy ($E_{Se\cdots S}$) versus the electron density at bond critical points ($\rho_{Se\cdots S}$)

Moreover the Se-S interaction leads to the formation of a five-membered ring (involving the sulfur-bound methine carbon and two carbon atoms of the aromatic ring, together with sulfur and selenium) as indicated by the presence of ring critical points (rcp) for all compounds with the exception of the methylselenide **5** (see Table 3), for which again the presence of this interaction is questionable.

The Laplacian of the electron density ($\nabla^2\rho_{Se\cdots S}$) represents the curvature of the electron density in the three-dimensional space at the BCP. A negative value of the $\nabla^2\rho$ indicates a local concentration of the electron density and is usually related to covalent bonds. A positive value of $\nabla^2\rho$, on the contrary, shows that a local depletion of the electron density occurs at the BCP, suggesting a closed-shell (electrostatic) interaction.

The results of the AIM analysis relative to the Laplacian of the electron density at the BCP for the Se$\cdots$S interaction ($\nabla^2\rho_{Se\cdots S}$, Table 3) show in all the cases a positive sign, suggesting a dominant electrostatic character. These results are in contrast with the previous conclusions derived from NBO analysis and with the atomic charges derived from NPA. Similar results, with positive values of the Laplacian $\nabla^2\rho$ for Se$\cdots$O and Se$\cdots$N interactions, with strong evidences of a dominant covalent character, have been previously reported by Tomoda and Mugesh.[4f,6b]

It has been proposed that the total energy density at the BCP H (H = G + V, where G is the electronic kinetic energy density and V is the electronic potential energy density) is a better parameter to understand nonbonded interactions.[20a] The values of $H_{Se\cdots S}$ (see Table 3) are in all the cases negative for compounds **1**-**3**, supporting the hypothesis of a dominant covalent character for Se$\cdots$S interaction in these compounds. Compounds **4** and **5** show in almost all the cases a slightly positive value for $H_{Se\cdots S}$, but these results are too small in the absolute value to be significant and

this observation suggests once again that this interaction does not exist or is very small in diselenide **4** and selenide **5**. The correlation plot of the total electron density at the BCP ($H_{Se\cdots S}$) against the distance between Se and S atoms is reported in Figure 5. Total electron density $H_{Se\cdots S}$ becomes more negative, as expected, with the decrease of Se···S distance and thus with the strengthening of the Se···S interaction.
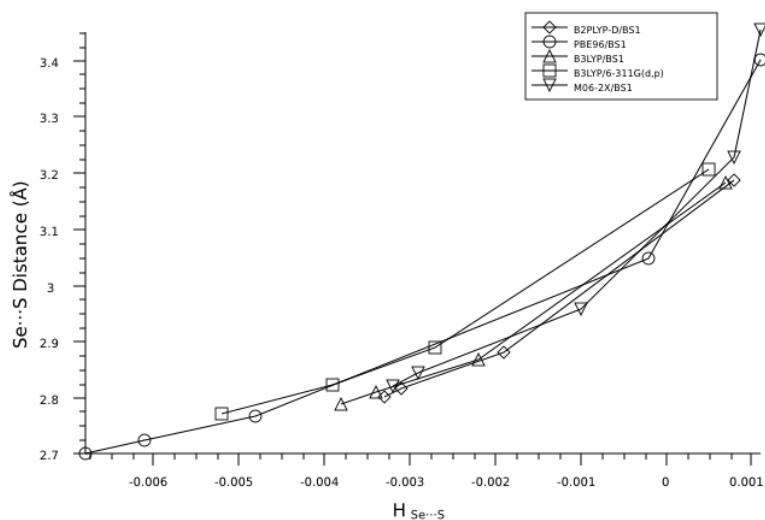
Figure 5 Plot of Se-S distance versus the total energy density at the BCP (H)

To better understand Se···S interactions the AIM dual-parameter analysis proposed by Nakanishi has also been employed.[26] The plot of $H_{Se\cdots S}$ versus $\nabla^2\rho_{Se\cdots S}$ is reported in Figure 6. All the points, with the exceptions of results for compounds **4** and **5**, fall in the fourth quadrant, suggesting that Se···S interaction has both characteristics of shared-shell and closed-shell interactions. Similar results were found by Mugesh and co-workers for related Se···N interactions.[6b]

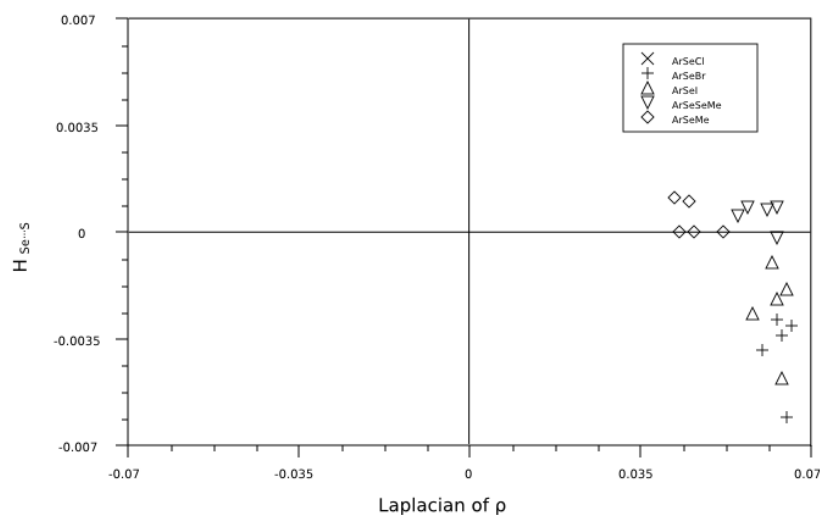**Figure 6** Plot of $H_{Se\cdots S}$ versus $\nabla^2\rho_{Se\cdots S}$ at the bcp

4. Conclusions

The nature and the strength of Se···S interactions in electrophilic selenenylating reagents as well as in related diselenide and methylselenide have been studied by means of quantum chemical techniques using five combinations of density functionals and basis sets. The strength of this interaction is strongly dependent on the nature of the group bound to selenium, decreasing in the order ArSeCl (**1**) > ArSeBr (**2**) > ArSeI (**3**), and is very small, if present, in diselenide ArSeSeMe (**4**) and selenide ArSeMe (**5**). NBO analysis suggests that this interaction has a covalent character and derives from a donation of the electron density from the lone pairs of sulfur (n_S) to the antibonding orbital of the Se-X bond (σ^*_{Se-X}). AIM analysis, and in particular the negative values of total energy density $H_{Se···S}$ found for compounds **1**-**3** at all the level of theories further support these findings.

Acknowledgments

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